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Studies on explosive reactions of tetrafluoroethylene and acetylene with oxygen or air : part I. explosive phenomena of gaseous tetrafluoroethylene-oxygen or air mixtures

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Part I Explosive Phenomena of Gaseous Tetrafluoroethylene-Oxygen or Air Mixtures

Results

a) Explosive reactions of tetrafluoroethylene-oxygen mixtures

In order to determine the temperature at which the reaction between tetrafluoroethylene and oxygen would occur, a definite quantity of the gaseous mixture at fixed compositions being contained in the reaction vessel at room temperature, the temperature of the vessel was raised at a definite heating rate (about 1 deg./min.), and pressure and temperature were measured every 10 minutes by the manometer M_3 and thermocouple T. Fig. 1. 1 shows these pressure-temperature curves

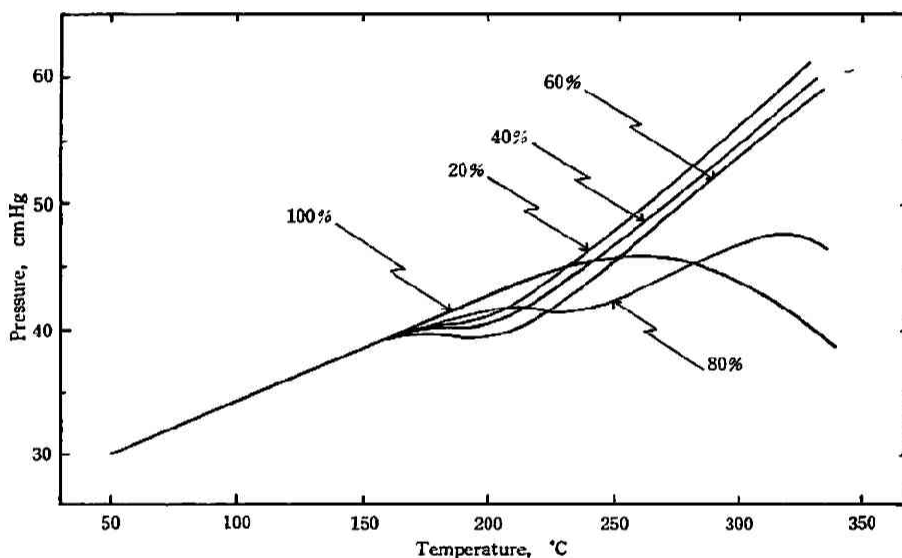


Fig. 1. 1 Temperature dependence of pressure of $C_2F_4-O_2$ mixtures when heated at a definite heating rate

at specified compositions. The curve for pure tetrafluoroethylene does not exhibit any pressure decrease until about 250°C, whereas the other curves show slight pressure decreases deviated from the straight line shown in the case of pure tetrafluoroethylene at a temperature of, say, 200°C, which may suggest the occurrence of reactions between tetrafluoroethylene and oxygen. We performed our experiments in the anticipation that explosion temperature might be near 200°C. Thus the conditions of temperature and pressure that give rise to explosion at the compositions of 20, 40, 60 and 80% C_2F_4 can be obtained by the experimental method described above and are shown in Fig. 1. 2. At the temperature above 350°C, the curves become nearly parallel to the temperature axis and the asymptotic pressures are approximately 5 cm Hg.

The pressure-composition diagrams of explosion limits at various temperatures and the temperature composition diagrams of explosion limits at various pressures are shown in Figs. 1. 3 and 1. 4 respectively. The curves shown in these figures exhibit the minima at the composition of

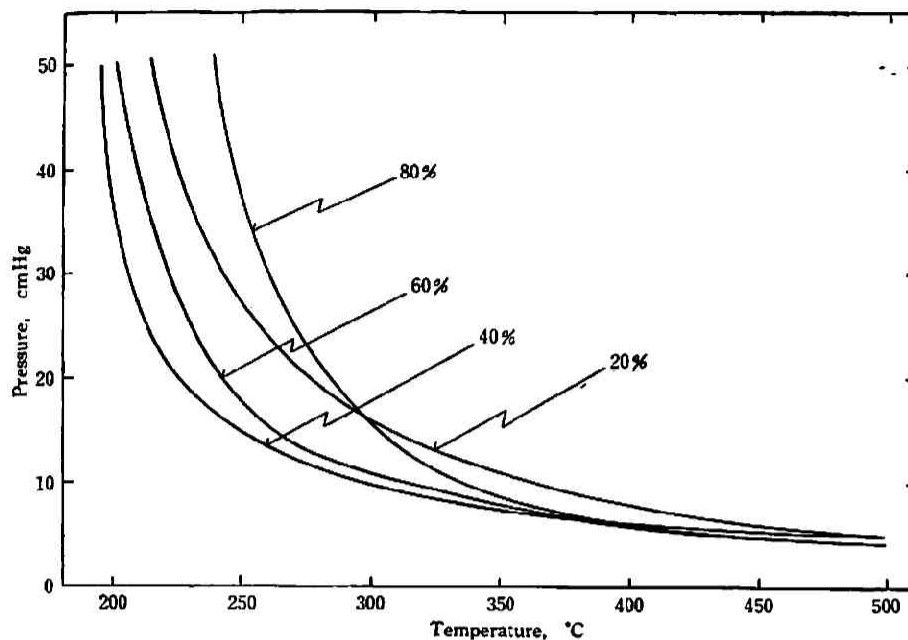


Fig. 1.2 Relations between temperature and pressure of explosion limits at specified compositions in $C_2F_4-O_2$ mixtures

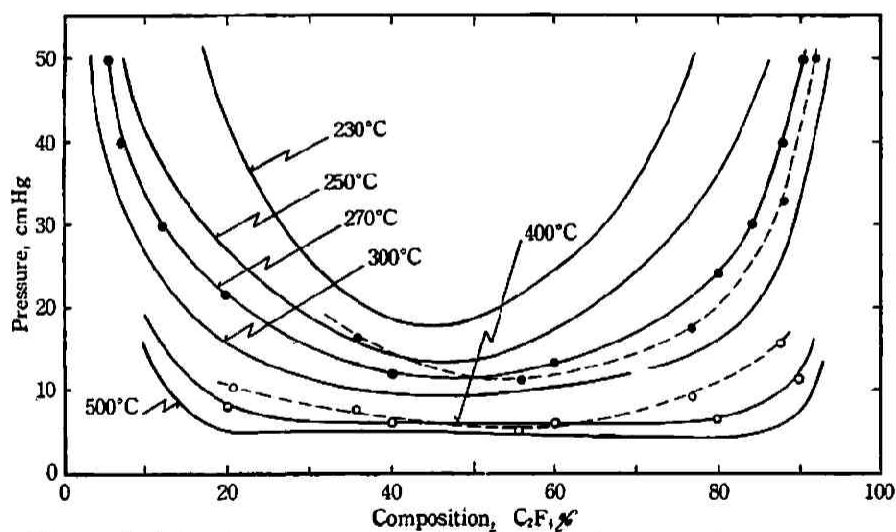


Fig. 1.3 Relations between pressure and composition of explosion limits at specified temperatures in $C_2F_4-O_2$ mixtures (Broken lines represent the data calculated from the limits of C_2F_4 -air mixtures, illustrated in Considerations. ● 270°C, ○ 400°C)

about 50%. The lowest explosion pressure and temperature are about 5 cm Hg and 196°C respectively.

To examine the wall effects, experiments were made for the mixture of C_2F_4 (50%)- O_2 in

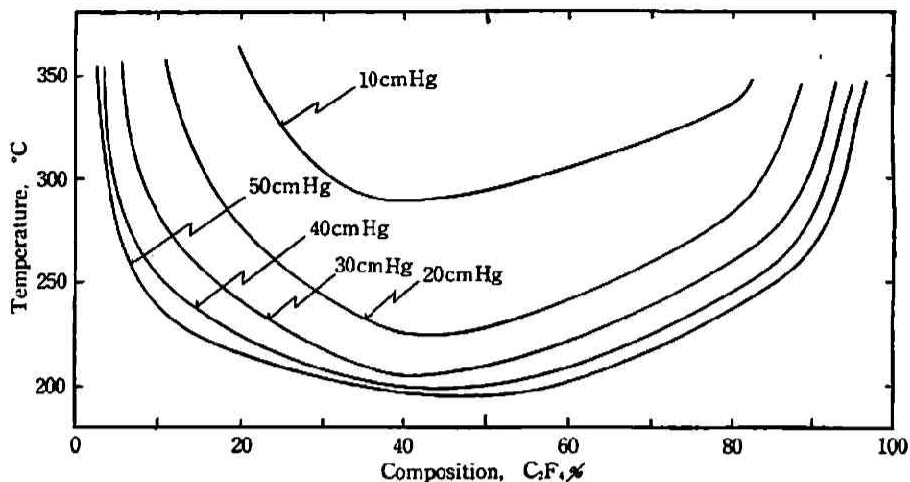


Fig. 1.4 Relations between temperature and composition of explosion limits at specified pressures in C_2F_4 - O_2 mixtures

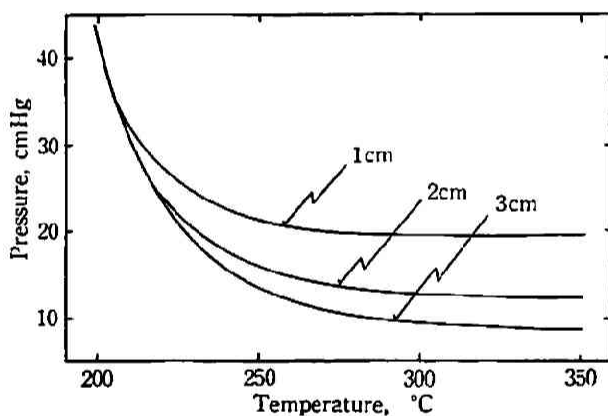


Fig. 1.5 Effect of vessel diameter on explosion limits in C_2F_4 (50%)- O_2 mixture

the vessels having diameters of 1, 2 and 3 cm. The results are represented in Fig. 1.5. At lower temperatures the curves of explosion limits are nearly coincident, but at higher temperatures the decrease in vessel diameter causes the explosion limits to be higher, and the tendency is more remarkable in the vessel of 1 cm diameter than in that of 2 cm diameter.

The colors of explosion flames, as shown in Fig. 1.6, change in the order of orange, yellow and blue with the decreasing of the percentage of tetrafluoroethylene and have relation to reaction products, that is, orange flames usually deposit carbon on the vessel surface, while blue flames are accompanied with white products. Pale-blue flames observed near the explosion boundaries propagate at a slow speed along the long axis of the vessel. When we make use of quartz vessels at higher temperatures and lower pressures, feeble green flames are observable, which may be attributed to some oxidation reaction since in pure tetrafluoroethylene without oxygen these flames are not observed.

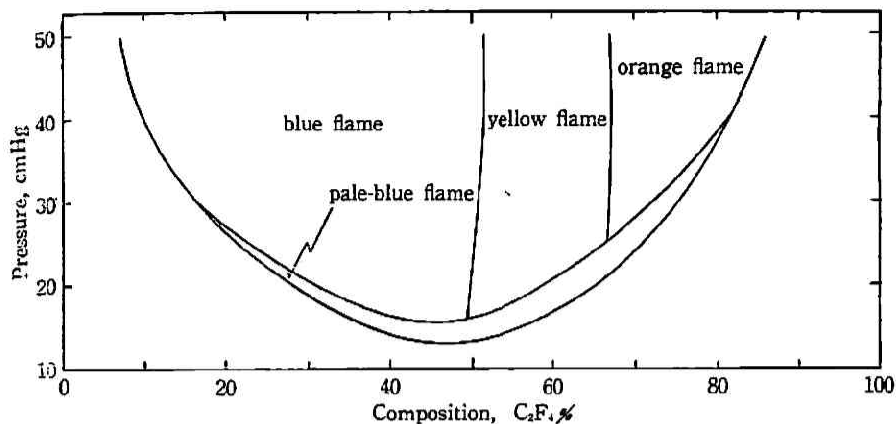
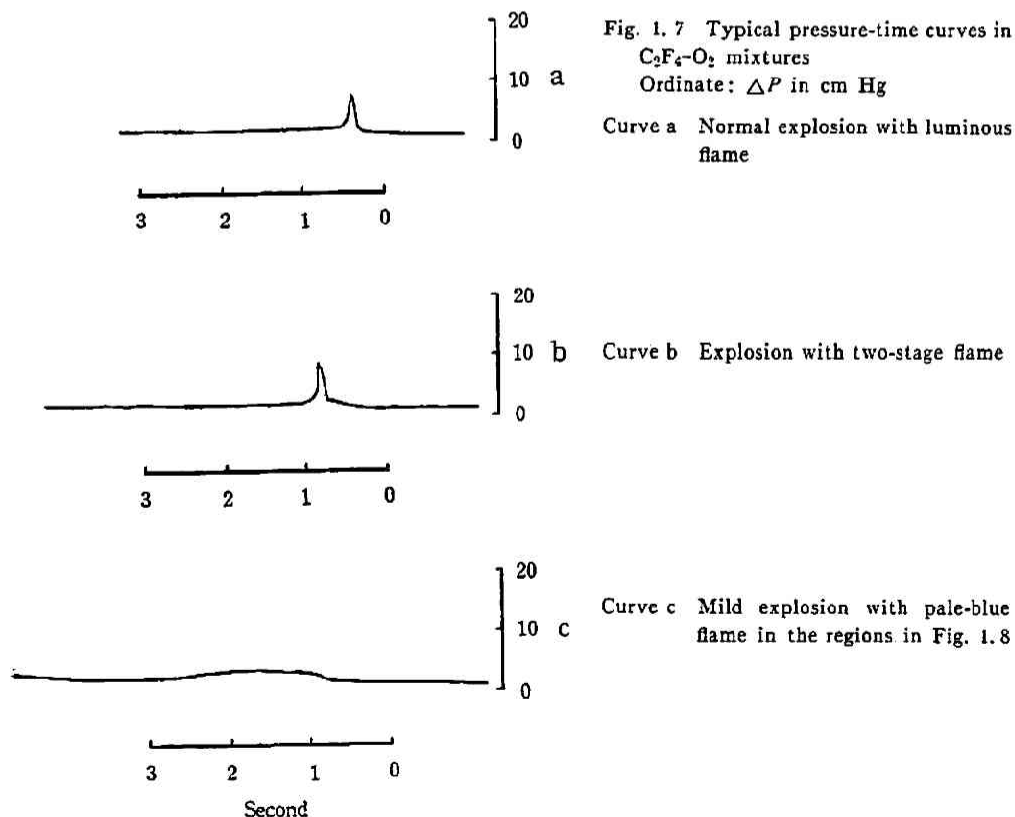


Fig. 1.6 Colors of explosion flames at 250°C in the vessel of 3 cm diameter ($C_2F_4-O_2$ mixtures)

Typical pressure-time curves recorded by the strain gauge and the ink writing oscillograph are shown in Fig. 1.7. Curve a indicates a very rapid increase of pressure with luminous orange or blue flash and this corresponds to a normal ignition. Curve b represents two-stage



ignition in which pale-blue flame occurred near the wall of the vessel changes momentarily into luminous orange or blue flash. Curve c shows mild pressure increase due to slower reaction than the case of curve a or b and is accompanied with pale-blue flame found under the conditions near the explosion limits and has slow propagation of flame (several centimeters per second).

The regions of pale-blue flames determined by the automatic mechanical pressure recorder are given in Fig. 1. 8. Within the temperature range of 250–290°C, the higher the temperature,

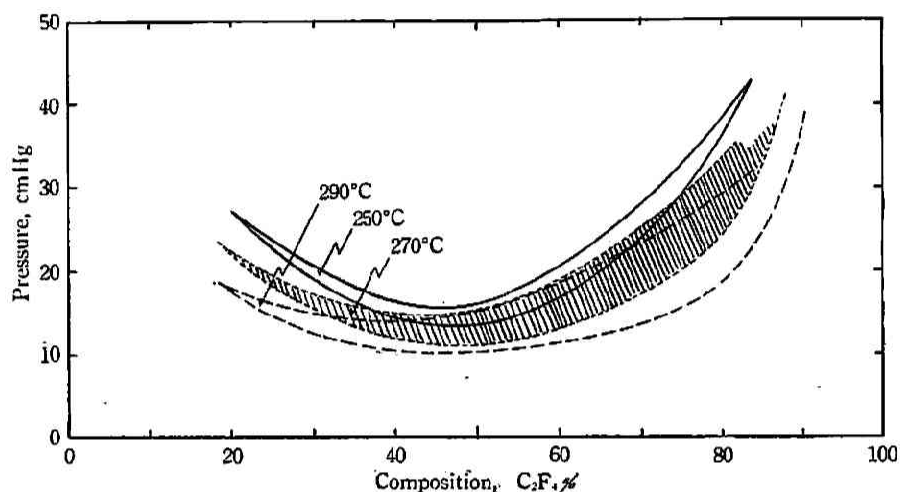


Fig. 1. 8 Regions of pale-blue flames in $C_2F_4-O_2$ mixtures at temperatures of 250°, 270° and 290°C

the wider becomes the pressure range of pale-blue flame at specified compositions.

In addition to these experiments described above, several preliminary observations were performed as follows.

Observation of explosions has been done for 5 minutes immediately after the admission of the gaseous mixtures. This is based on the fact that in the explosive regions $C_2F_4-O_2$ mixtures explode within 2 minutes from the admission, and that outside the explosion regions they do not explode during the continuous measurement of 50 hours by the automatic pressure recorder.

Gases of tetrafluoroethylene and oxygen being mixed in a reservoir, they were kept generally more than 12 hours for the completion of mixing. The reservation is enough for mixing because mixtures kept in the reservoir at room temperature for a week, a month and half a year, give almost the same explosion limits as the mixture reserved for 12 hours.

It is sometimes found that the reaction products adhered to the inner surface of the vessel affect the explosion limits, that is, white products formed from rich oxygen mixtures will often widen the explosion area, while the carbon products from poor oxygen mixtures have a tendency to contract the area. So in order to remove these effects, the authors heated the reaction vessel at about 350°C evacuating about half an hour and made use of it several times. When the virgin surface of a reaction vessel is used, reproducible results are obtained after the first explosion.

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These cares are taken to obtain satisfactory results.

Mercury manometer M_3 was sometimes used together for the measurement of pressure changes, and so for the purpose of testing the effect of mercury upon the explosion, experiments were carried out in hot vessels into which a few drops of mercury had been poured. It was recognized that mercury retarded the explosion to some extent. In the present experiments, however, the effect can be neglected owing to the low vapor pressure (1.2×10^{-3} mm Hg) at room temperature.

b) Explosive reactions of tetrafluoroethylene-air mixtures

The explosion limits were determined for tetrafluoroethylene-air mixtures by the same experimental method described above.

Figs. 1. 9 a and b show the explosion limits of temperature-pressure diagrams at specified

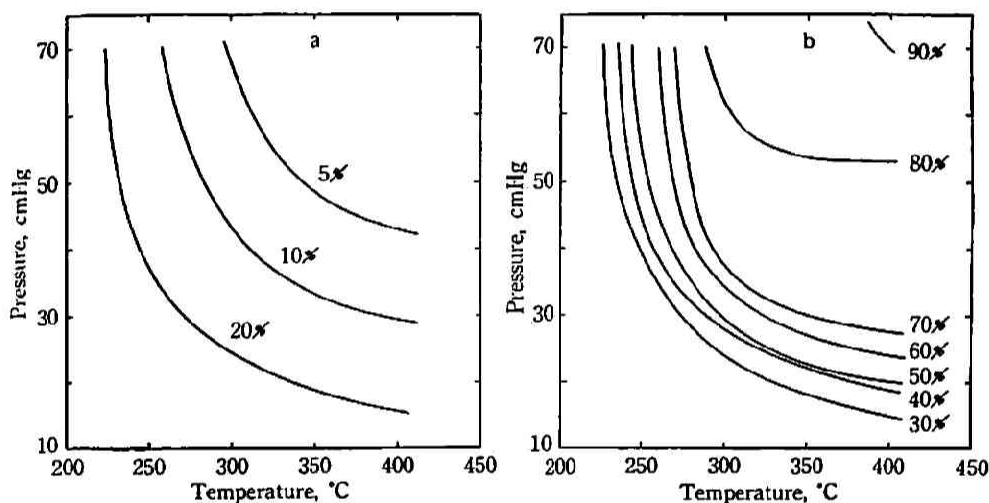


Fig. 1. 9 a, b Relations between temperature and pressure of explosion limits at specified compositions in C_2F_4 -air mixtures

compositions. At lower temperature, the curves become almost parallel to the pressure axis and are similar to hyperbolas. The pressure-composition diagrams of the explosion limits at definite temperatures, and the temperature-composition diagrams of the explosion limits at definite pressures are shown in Figs. 1. 10 and 1. 11 respectively. The limits exhibit the minima at a composition of some 20% C_2F_4 . The lowest explosion pressure and temperature are about 15 cm Hg and $222^\circ C$ respectively.

The explosion limits in the vessels of different diameters of 1, 2 and 3 cm at 20% C_2F_4 are given in Fig. 1. 12. The narrower the diameter of the vessel (i. e. the larger the ratio of surface to volume), the higher become the explosion limits, and this tendency is more remarkable in the vessel of 1 cm diameter than in that of 2 cm diameter.

The colors of explosion flames are almost the same as those of $C_2F_4-O_2$ mixtures, that is, they are generally found to be pale-blue, luminous blue, (orange) yellow, orange flames and two-stage flames the color of which changes from pale-blue into luminous blue or orange.

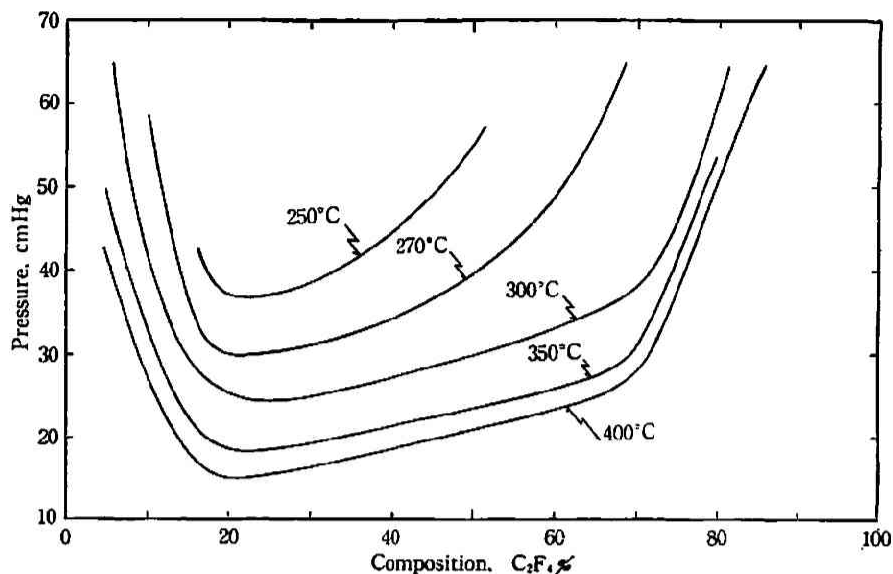


Fig. 1.10 Relations between pressure and composition of explosion limits at specified temperatures in C₂F₄-air mixtures

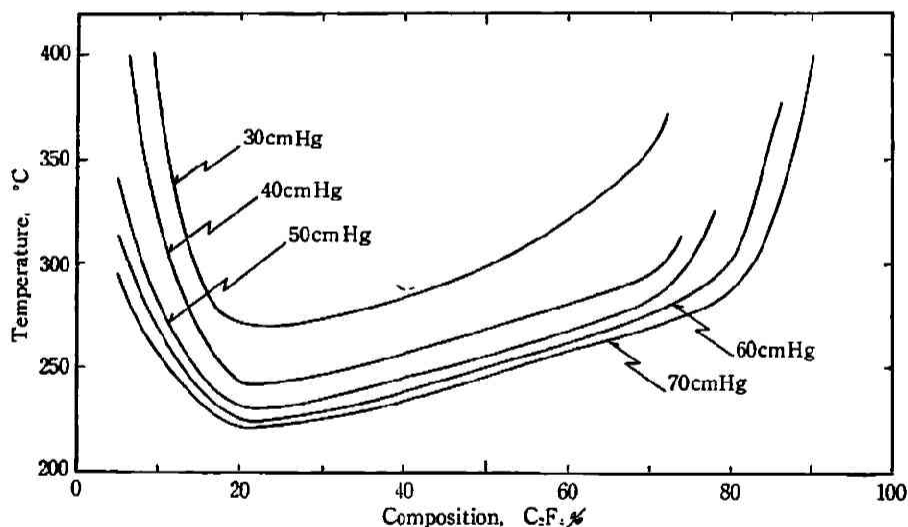


Fig. 1.11 Relations between temperature and composition of explosion limits at specified pressures in C₂F₄-air mixtures

The reaction products after the explosion reaction consisted chiefly of white substances (probably polymerization products) and little of carbon contrary to the case of C₂F₄-O₂ mixtures.

The typical changes of pressure with time recorded by the ink writing oscillograph are depicted in Fig. 1.13. Curve a shows an abrupt rise of pressure due to a normal explosion reaction with luminous blue or orange flame. Curve b corresponds to a two-stage ignition in which a pale blue flame occurring at the beginning is immediately changed to either a luminous

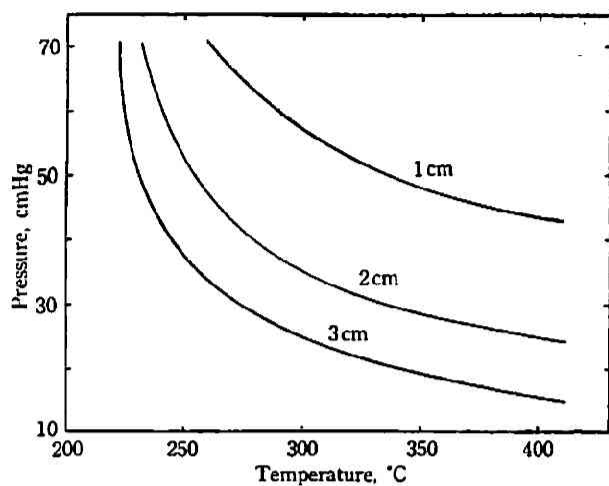


Fig. 1.12 Effect of vessel diameter on explosion limits in $C_2F_4(20\%)$ -air mixture

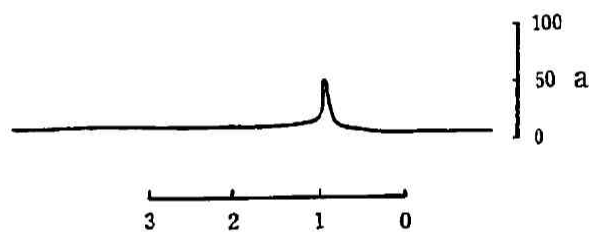
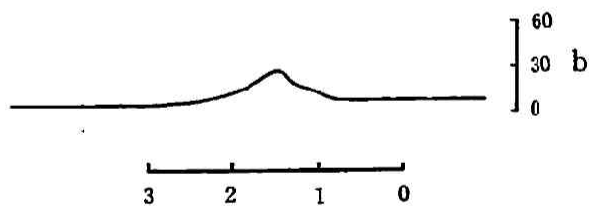
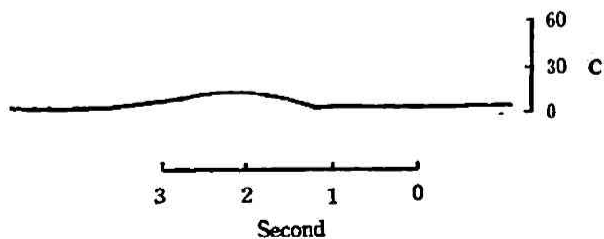


Fig. 1.13 Typical pressure-time curves in C_2F_4 -air mixtures
Ordinate: ΔP in cm Hg

Curve a Normal explosion with luminous flame



Curve b Explosion with two-stage flame



Curve c Mild explosion with pale-blue flame in the region in Fig. 1.14

blue or orange flame chiefly according to the composition of mixtures. Pressure increases of the second stages are often found to be more violent than that shown in this curve. Curve c represents a mild explosion with a feeble pale-blue flame.

The region where the pale-blue flame (the case of curve c) made its appearance at 290°C was determined by the automatic pressure recorder together from the observation of flame is shown in Fig. 1. 14. In comparison with Fig. 1. 8 it is found that with all compositions the

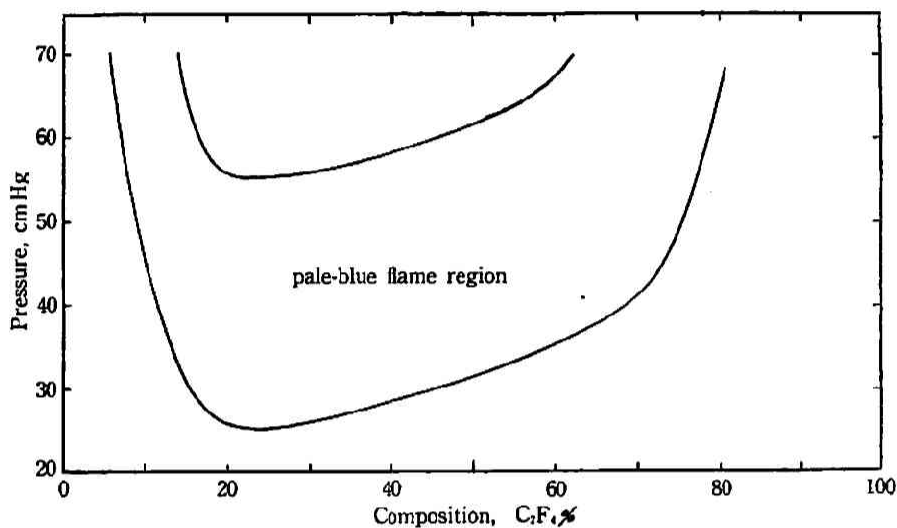


Fig. 1. 14 Pale-blue flame region in C₂F₄-air mixtures at 290°C

pressure ranges between the upper and the lower limits of the pale-blue flame region of the C₂F₄-air mixtures are much wider than those of C₂F₄-O₂ mixtures.

Considerations

In order to elucidate the effect of the foreign gas N₂, the limiting explosion pressures and compositions of C₂F₄-air mixtures at temperatures of 270°C and 400°C were converted into those of C₂F₄-O₂ mixtures by calculation subtracting the partial pressures of nitrogen. These calculations give the broken lines in Fig. 1. 3 which shift little from the corresponding full lines, and lead to the conclusion that the effect of nitrogen should be negligible.

Concerning the pale-blue flame region, however, the different result is obtained from the consideration that at the composition of equal mole ratio of C₂F₄ to O₂ with the mixtures of C₂F₄-O₂ and C₂F₄-air, that is, C₂F₄ (55%)-O₂ and C₂F₄ (20%)-air, the pressure ranges of pale-blue flames in Fig. 1. 8 and in Fig. 1. 14 are 6cm Hg and 10.8cm Hg respectively if the nitrogen pressure of the latter is removed. The pressure range becomes much wider than the increase in the pressure due to the addition of nitrogen.

Pale-blue flames in these regions have the properties that (1) the color is pale-blue, (2) the speed of flame propagation is slow (several centimeters per second), (3) pressure increase

accompanied is slight and mild, and the variation with time is smooth and (4) the phenomena of two-stage ignitions being observed under slightly severer conditions than those of pale-blue flames, it seems that pale-blue flames occur in the early stages of normal flames. Though these properties may be those of cool flames, such closed areas as generally found on cool flames are not obtained in the present experiments because the upper limits of pale-blue flame regions cannot be determined by the oscillograph owing to very short induction period at higher temperatures.

Detailed observation of the curves of pressure change with time in Figs. 1. 7 and 1. 13 gives the fact that in the initial stages of explosions the pressure curves a are convex to the time axis and the curves c corresponding to the mild explosions with pale-blue flames are concave to the axis. These facts might be understood⁴⁾ if assumed that such reactions as curves a proceed by branching chains and such as c by non-branching straight chains, whereas as to the cool flame reaction, there is a view that it proceeds by straight chains⁵⁾.

If the induction period is assumed to be the time necessary for the production of a definite concentration of intermediates, the following relation can be obtained between absolute temperature T and induction period τ^* .

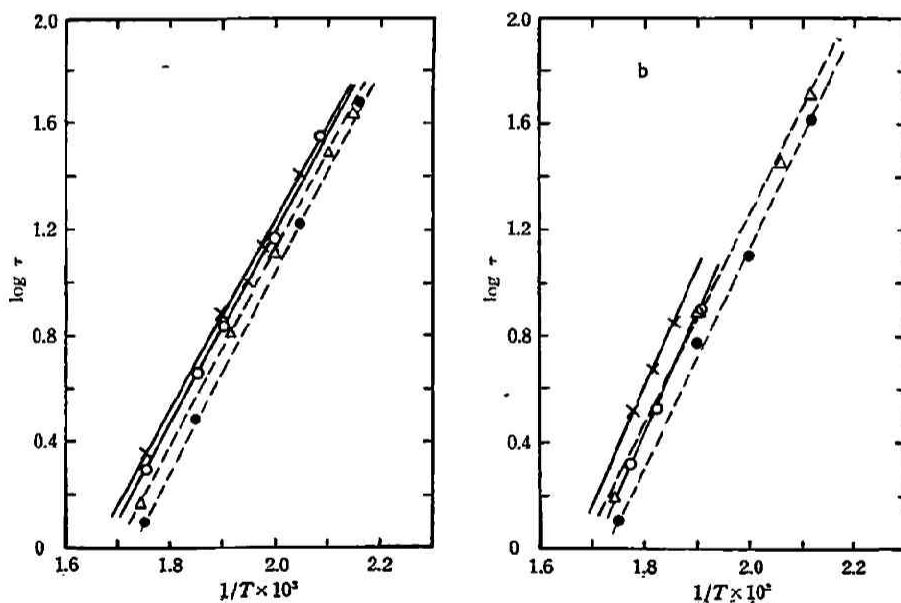


Fig. 1.15 Relations between $\log \tau$ and $1/T$ in $C_2F_4-O_2$ mixtures

a $\left\{ \begin{array}{l} \times \text{ 20\% } C_2F_4, \text{ 30 cm Hg} \\ \circ \text{ 20\% } C_2F_4, \text{ 40 cm Hg} \\ \triangle \text{ 60\% } C_2F_4, \text{ 30 cm Hg} \\ \bullet \text{ 60\% } C_2F_4, \text{ 40 cm Hg} \end{array} \right.$

b $\left\{ \begin{array}{l} \triangle \text{ 40\% } C_2F_4, \text{ 30 cm Hg} \\ \bullet \text{ 40\% } C_2F_4, \text{ 40 cm Hg} \\ \times \text{ 80\% } C_2F_4, \text{ 30 cm Hg} \\ \circ \text{ 80\% } C_2F_4, \text{ 40 cm Hg} \end{array} \right.$

4) J. Osugi, *This Journal, Commemo.* Vol. 76 (1946)

F. S. Dainton, *Chain reaction*, Methuen, p. 82 (1956)

5) B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press Inc., p. 142 (1951)

* Assuming that the rate of the reaction producing intermediates is first order in the equation of Arrhenius $k=Ae^{-K/RT}$, τ is proportional to $\frac{1}{k}$. From these relations, the equation (1) is derived.

$$\ln \tau = \frac{E}{RT} + \text{constant.} \quad (1)$$

This relation, as shown in Figs. 1. 15 and 1. 16, holds both with $\text{C}_2\text{F}_4\text{-O}_2$ and with $\text{C}_2\text{F}_4\text{-air}$

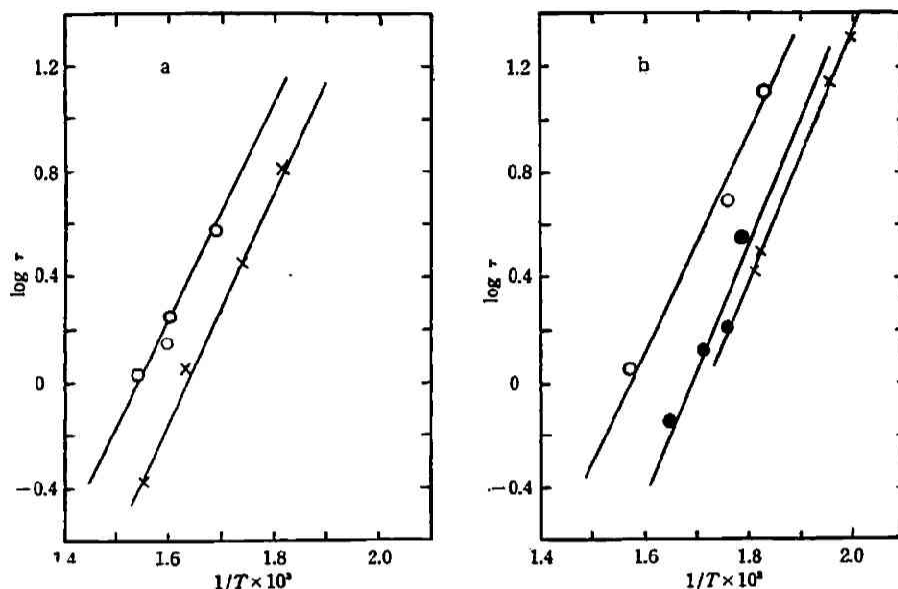


Fig. 1. 16 Relations between $\log \tau$ and $1/T$ in $\text{C}_2\text{F}_4\text{-air}$ mixtures

a { \bigcirc 5% C_2F_4 , 50 cm Hg
 \times 10% C_2F_4 , 50 cm Hg

b { \bigcirc 20% C_2F_4 , 30 cm Hg
 \bullet 80% C_2F_4 , 70 cm Hg
 \times 20% C_2F_4 , 70 cm Hg

Table 1 Activation energies
(vessel diameter: 3 cm, $\text{C}_2\text{F}_4\text{-O}_2$ mixtures)

initial pressure cm Hg	composition C_2F_4 %	activation energy kcal/mole
30	20	17.8
30	40	18.1
30	60	17.6
30	80	22.6

Table 2 Activation energies
(vessel diameter: 3 cm, $\text{C}_2\text{F}_4\text{-air}$ mixtures)

initial pressure cm Hg	composition C_2F_4 %	activation energy kcal/mole
30	20	18.5
50	5	18.6
50	10	19.8
70	20	21.7
70	80	21.4

mixtures. Calculation of apparent activation energies from the slopes of straight lines in these relations gives the values in Tables 1 and 2. With the mixtures of C_2F_4 (50%)– O_2 and C_2F_4 (20%)–air which have nearly the same mole ratios of C_2F_4 to O_2 , the values of activation energies have little difference.

In a thermal explosion the condition of which is that the rate of temperature rise due to evolution of reaction heat exceeds the rate of cooling, the following relation can be derived⁶⁾.

$$\ln \frac{P}{T} = \frac{E}{2RT} + \text{constant}. \quad (2)^*$$

With the mixtures of C_2F_4 – O_2 and C_2F_4 –air the plots of $\log \frac{P}{T}$ against $\frac{1}{T}$ give nearly straight lines of slopes equal to $\frac{E}{2RT}$ only within the narrow temperature range. And the values of E calculated from the slopes of straight lines are nearly 10 kcal/mole smaller than those shown in Tables 1 and 2. So the relation (2) does not hold satisfactorily.

As to the pressure limits of C_2F_4 –air mixtures at definite temperatures if designated the partial pressures of tetrafluoroethylene, oxygen and nitrogen as $P_{C_2F_4}$, P_{O_2} and P_{N_2} respectively, the values of $P_{O_2} P_{C_2F_4} \left(1 + \frac{P_{N_2}}{P_{O_2} + P_{C_2F_4}}\right)$ are almost constant for all compositions. Moreover, examining the effects of vessel diameters, the following empirical formula is obtained and the examples of the values are shown in Table 3.

$$P_{O_2} P_{C_2F_4} \left(1 + \frac{P_{N_2}}{P_{O_2} + P_{C_2F_4}}\right) d^{\frac{3}{2}} = \text{constant}. \quad (3)$$

Table 3 Values of $P_{O_2} P_{C_2F_4} \left(1 + \frac{P_{N_2}}{P_{O_2} + P_{C_2F_4}}\right) d^{\frac{3}{2}}$

temperature °C	vessel diameter cm	$P_{C_2F_4}$ cm Hg	P_{O_2} cm Hg	$P_{O_2} P_{C_2F_4} d^{\frac{3}{2}} \left(1 + \frac{P_{N_2}}{P_{O_2} + P_{C_2F_4}}\right)^{**}$
270	1	13.7	11.0	4.2×10^2
	2	8.5	6.8	4.6 "
	3	6.1	4.9	4.3 "
300	1	11.4	9.1	2.9 "
	2	7.0	5.6	3.1 "
	3	4.9	3.9	2.8 "
350	1	9.5	7.6	2.0 "
	2	5.6	4.5	2.0 "
	3	3.7	3.0	1.6 "

Assuming $P_{N_2}=0$ in the equation (3), it becomes

$$P_{O_2} P_{C_2F_4} = \text{constant}. \quad (4)$$

This relation, however, is found not to be the case with C_2F_4 – O_2 mixtures. In order to

6) N. Semenov, *Z. Physik*, 48, 571 (1928)

* P and T express the limiting explosion pressure and temperature.

** Units of pressure and diameter are cm Hg and cm respectively.

explain the relation (3) by the chain mechanism of hydrocarbon combustions, it should be necessary to modify the elementary reactions assumed in the derivation of equation (3)⁷⁾ considering that the triple collision process might be included. It may be considered that inapplicability of the relation (4) to $C_2F_4-O_2$ mixtures is due to the lower total pressures and to the different influence of the pressures upon the mechanism of chain branching, propagating and terminating processes.

Compared with equation (2), the relation (3) may be rather applicable to this explosion.

Part II Explosive Phenomena of Gaseous Acetylene-Oxygen Mixtures

Results

The explosion limits of gaseous $C_2H_2-O_2$ mixtures were determined at specified compositions, using glass reaction vessels of 1 cm, 2 cm and 3 cm diameters, and are shown in Figs. 2.1 a (95% C_2H_2), 2.1 b (90% C_2H_2), 2.1 c (80% C_2H_2) and 2.1 d (70% C_2H_2). The experiments on the

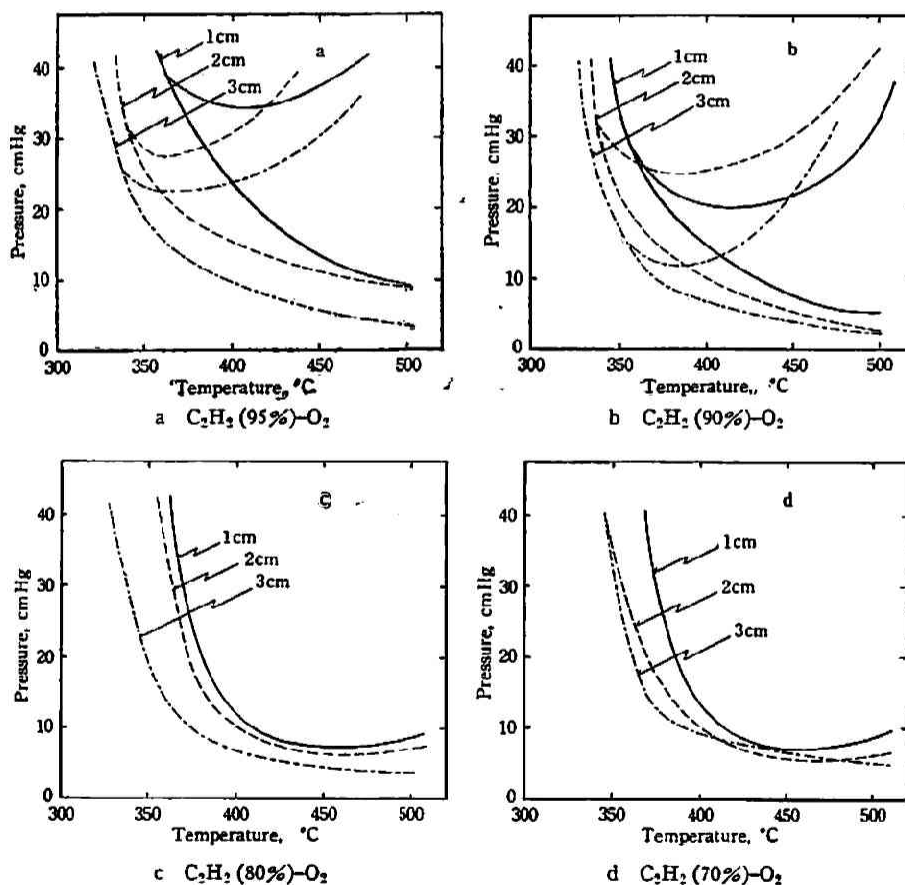


Fig. 2.1 a, b, c, d Relations between temperature and pressure of explosion limits at specified compositions

7) K. J. Laidler, *Chemical Kinetics*, McGraw-Hill Book Co., p. 319 (1950)